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(54) **Glucomannan/polyhydric alcohol composition and film prepared therefrom.**

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EP-A- 0 109 269
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CHEMICAL ABSTRACTS, vol. 97, 1982, page 487, abstract no. 4931e, Columbus, Ohio, US

CHEMICAL ABSTRACTS, vol. 100, 1984, page 530, abstract no. 137715q, Columbus, Ohio, US

PATENT ABSTRACTS OF JAPAN, vol. 6, no. 98 (C-106)[976], 8th June 1982

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Description

BACKGROUND OF THE INVENTION

The present invention reletes to a composition heving a complex network structure that is formed by mixing glucomannan and optionally another natural polysaccharide with e polyhydric alcohol such as glycerin or a concentrated solution thereof in the presence of absence of an alkali. The present invention also relates to a film prepared from this composition.

The composition of the present invention can be dissolved in water to form a viscous solution. A film formed of this composition is water-resistant and may be givan graater strengthand haat-resisting property. The film finds utility in various applications such as edible films, semipermeable membranes for separating low-molecular weight materials from those having high molecular weights ; wound dressings, and the shells of soft capsules.

The principal use of glucomannan has baen to produce konjak by reacting it with an alkali in an aqueous solution, then heating the reaction product to form a gal. Tha gel formed bythis mathod has an inhomogeneous structure and finds no utility other than as konjak. Other natural polysaccharides have been used in an aqueous solution as thickeners, gelling agents, water retainers, stabilizers, dispersants, amulsifiars, binders, etc.

Compounds having multiple hydroxyl groups as exemplified by polyhydric alcohols, sugar alcohols, monosaccharides, dissaccharidas and oligosaccharidas hava been used solaly as additivas such as sweeteners, humectants, softening egents and plasticizers. Moreover, thesa compounds have been used singly and no aftempt has been made to allow the natural polysaccharidesto react directly with polyhydric alcohols in the presence of e small amount of water.

Edible films currently available include starch-based waters, gelatin-based collagen film, and pullulan films. All of these films except those based on geletin lack rasistance to watar. Even gelatin films lack high resistance to acid, alkalies and heat. Films formed of cyclodaxtrina or special protains obtained by extracting nucleic acids, cell membranes, etc. from yeasts ere expensive and their high cost is not justified by corresponding improvements in water resistance, heat resistance and strength.

In tha production of smoked meet products such as hams and sausages, semipermeable membranes such as thosa made of animal guts, regenarated cellulose or cellulose derivatives are used to allow the fragrant and seasoning components in the amoke to penetrate into the meat. However, the supply of animal guts is not abundant and, in addition, they lack strength and are not uniform in size. Tha supply of regenerated cellulose and cellulose derivatives is also limited because strict regulations against pollubon has rendered the construction of new plants practically impossible.

Galatin has heratofora been used es the shall metereal of aoft capsules for cunfining drugs, flavors or saasonings but the user of gelatin is limited to applications whara oily substances are employed.

Electrolytes or low-molecular weight materials heve been separated from high-molecular weight matarials by such means es electrodialysis, reverse osmosis, and ion-exchange membrane technology. Howavar, these methods use a large number of electrodes or require high pressures so that the equipment for practicing these methods is becoming more and more complex. In order to desalt foods by these methods, large-sized equipmentis necessary and it often occurs that other seasoning componentsare eliminated as well as the sodium salt with tha result that the tasta of tha food la impaired.

In tha treatment of akin losses due to burns or othar extemal injurias, tha affectad area is temporarily covered to prevent loss of water or body fluids from the wound, or any exudate from the wound is desplaced to prevent bacterial infection so that the formation of granulations and the epidermis is promoted. The films which have baen used or attempted to be used for these purposes are formed of such materials as silicona rubbar, poly -E -caprolactona, poly (vinyl alcohol) , polyamino acids,fibrin membranes, collagen, polyurethane and pigskin.

However, freeze-dried pigskin and othar polyamino acid based wound dressings ara all made of polypeptides which are subject to biochemical decomposition. In order to avoid tha adversa effects of the degredation products which are liberated, these wound dressings heve to be replaced at short intervals, typically every other day. However, replacement of the wound dressing involves much pain for the patient. Furtharmora, the film itself has insufficient strangth to attain satisfactory covarage. Wound dressings made of synthetic resins such as polyurethane and allicona rubber do not heve sufficient affinity for tha wound surface to achieve satisfactory permeabon to oxygen and water. Nomal skin generally allows water to be evaporated in an approximate emount of 350g/m^2 per day, but it has been difficult to prepara synthetic resin films that exhibit this amount of water evaporetion and which yet has sufficient strength.

It has been proposad to prapare a composite wound dressing by lamineting a polyamino acid based

film with a synthetic resin film but this composite film still suffers from the defects of the respective film components.

SUMMARY OF THE INVENTION

The present inventors have found that if glucomannan, either independently or in combination with other natural polysaccharides, is mixed with a compound heving multiple hydroxyl groups or with e concentrated solution thereof in the presence of absence ofan alkali, the respective components react with each other to form a composition having a dense three-dimensional structure. The present inventors have also found that e viscous solution formed by dissolving this composition in weter has unique physicochemical properties that have been unattainable by glucomannan, other natural polysaccharides or polyhydric alcohols, and that various products having the cheracteristics shown below can be prepared from this composition. The present invention has been accomplished on the basis of these findings.

Firstly, edible films having desirable properties s uch as water resistance, heat rasistance and strangth can be prepared from the above-described viscous aqueous solution either directly or after being mixed with other foods or food materials. The so prepared films may be eaten as such or used as edible food packages.

Secondly, the viscous aqueous solution may be dried into film form and the resulting film may be used in the production of processed meat products (e.g. hams and sausages) as semipermeable membranes having sufficient strength and heet resistance to withstand smoking condition.

Thirdly, the viscous equeous solution may be processed to form a film thet is suitable for use as the shell of a soft capsule, and using this film, soft capsules capable of confining non-oily drugs, health foods, seasonings or flevors can be prepared.

Fourthly, the film made from the viscous aqueous solution also serves as a high-performance filter medium that is capable of efficient separation of low-molecular weight substances from high-molecular weight substances et reasonably low pressures.

Fifthly, the membrene formed by drying the viscous aqueous solution into film form is e superior wound dressing that achieves close contact with the skin and exhibits superior vapor and oxygen permeetion without undergoing any biodegradation during prolonged ettachment to the skin.

Sixthly, the viscous aqueous solution cools to provide a gel-like or semifluid foodstuff heving unique properties.

DETAILED DESCRIPTION OF THE INVENTION

The glucomannan used in the preparation of the composition of the present invention is the polysaccharide naturelly occurring in Amorphophallus Konlac K. Koch which is the rhizome of a plane belonging to Colocasia antiquorum; it is composed of particles referred to as idioblasts which range from 0.5 to 1.05 mm in length and from 0.37 to 0.5 mm in breadth. The chemical structure of glucomannan is a chain of a 1 : 2 mixture of glucose and mannose with acetyl and phosphate groups forming pendant ester linkages.

Illustrative polyhydric elcohols that can be used in the present invention are polhydric elcohole in the narrow sense of the term such as propylene glycol end glycerin. These polyhydric elcohols are liquid and may be directly used; however, because of their high hygroscopicity they contain water and are in the form of concentreted equeous solutions. Moreover they can be used as water solution of concentration in the range of 30 to 90 %. Illustrative sugar alcohols include sorbital, mannitol, maltitol, xylytol and saccharified products of reducing sugar. Illustrative monosaccharides include glucose, fructose, galactose and xylose. Illustrative disaccharides are saccharose, maltose and lactose. Starches such as sweet potato, potato and com that heve been decomposed with enzymas or acida are usable as oligosaccharidee, end include di-, tri-, tetre-, penta- and hexasaccherides. The polyhydric elcohols listed above, both in the broad and narrow sense of the term, which are in a powder form et ordinary temperetures, are used as aqueous solutions having concentrations in the range of 30-90 wt %, preferably 50-80 wt %, more preferable 65-75wt%.

Other naturel polysaccharides that may be used in the present invention include the following:

alginic acid which are intracellular polysaccharides in brown algae,

sodium alginete,

propylene glycol ester of alginic acid, end

egar;

carregeenan which ie an Intracelluler polysaccharide in red elgae and is hydrolyzed into D-gelectose end D-gelactose sulfate ester ;

locust bean gum which is a polysaccharide that is present in the seeds of leguminous locust bean and

carob and which is chiefly composed of glucomannen;

guar gum that is e polysaccharide present in the seed of leguminous guar and which is hydrolyzed into galactose and mannosa ;

tamarind seed polysaccheride which is a polyseccharide present in the seed of leguminous Tamarindus indica and which is hydrolyzed into glucose, xylose and galectose ;

pectin which is a generic term for a group of polysaccarides thet are the meterials of construction of the cell walls of plants such es fruit and vegitables and which are hydrolyzed in to galacturonic acid;

xanthan gum is a polyseccharide produced by the microorganism Xanthomonas campestria during fermantation in the present of glucose and other appropriate essential elements;

chitin which ia one kind of mucopolysaccharides;

pullulan which has a repeating unit of α -1,6 linkege derived from maltotriose ; end

cellulose,

cyclodextrin and

starches.

These natural polysaccharides are optionally used in amounts of 0.05 - 20 parts by weight, preferably from 0.1 to 10 parts by weight, per part by weight of glucomannan.

In the present invention, reaction is preferably carried out in the presence of an alkali. Ordinary inorganic or organic alkaline substancea mey be employed and auitable ones inclueded: sodium hydroxide, potassium hydroxide, calcium hydroxide, magnesium hydroxide, berium hydroxide, sodium carbonete, potassium carbonate, calcium carbonete, ammonium carbonate, magnasium carbonate, sodium bicarbonate, ammonium bicarbonate, basic amino ecids and amines. The addition of these alkalis is generally effective in providing films with improved strength and heat resistance.

Part of the glucomannan and optionally used natural polysaccharides may be replaced by proteins to provide compoaition which generally have improved heat resistance. Solutions of these compositions in warm water have good mouth feel and can be readily eaten. Illustretive proteins are soybeen protein, wheat protein, milk protein, egg white, collagen, decomposed collegen and microbial proteins. Decomposition products of these proteins, such as polypeptides and amino acids, may also be used.

The present invention is characterized by reacting glucomannan directly with at least one compound selected from among the polyhydric alcohols, sugar alcohola, monosaccharides, disaccharides end oligosaccharides. The component made of at least one compound selected from polyhydric alcohols, sugar alcohols, monosaccharides, disaccharides and oligosaccharides is used in an amount which ranges from 0.05 to 10 parts by weight, preferably from 0.10 to 5.0 parts by weight, more preferably from 0.15 to 1.0 part by weight, per part by weight of the powder component made of glucomannan and optionelly of ofher natural polysaccharides and proteins. Generally, a higher content of the polyhydric elcohol renders it difficult for e three-dimensional network to develop.

The reactants are mixed at a temperature ranging from 5 to 150 °C, preferably from 10 to 100 °C, more preferably from 20 to 80 °C. Mixing at low temperaturea will cause no problem because the intended reaction can be allowed to proceed satisfactorily by heating the mixture in a subsequent step such as drying. Generally, mixing at high temperetures provides a composition having a dense structure whereas a brittle composition having a coarse network results if low mixing temperatures are used.

The composition formed by mixing the starting materials described above is e powder that is usuelly moist to some extent. A solution of this composition in water is viscous and will solidify irreversibly when left to stand at ordinary temperetures, frozen, refrigerated or heated. The properties, in particular the strength, heat resistance and the temperature for dissolution in water, of the solidified product can be eltered by proper adjustment of the combination of the starting materiala used. Therefore, the solidified product can be used as a base for semifluid or gel-like foods such as jelly and jam. Films may be formed from the viscous solution by shaping it into a soldified form of a suitable thickness between 1 and 1,000 µm by any of the known techniquea auch as wet casting, freeze-drying and extrusion molding. Some of the filme formed by these methods are heat-resistant and heat-sealable. If desired, the viscous solution may be coeted or spreyed onto a foodstuff and dried to form en edible film on the food.

Films having thicknesses in the range of 1-1,000 µm, preferably 2- 300 µm, are useful as semipermeable membranes. In a more preferable embodiment, a thin and reinforced semipermeable membrane can be formed by preparing a thin fibrous product from an appropriate material such as paper, nonwoven fabric, woven fabric or net, then filling the voids in the fibrous product with the filter film of the present invention. Filling of the voids in the thin fibrous product may also be echieved by coating the film with the viscous solution or submerging the film in the solution, followed by drying of the film.

Filtration may be achieved by any known technique euch as simple filtering under grevity, ultrefiltration or reverse osmosis. The filter medium may be an assembly of hollow fibers or a module of a spirally wound

sheet.

In the simplest way, afoodstuff having high sodium chloride concentration is placed on top of the semipermeable membrene of the present invention which is in contact with an underlying water layer; in the absence of any applied pressure, sodium chloride end other low-molecular weight substances in the upper layer will permeate through the membrane to enter the underlying aqueous layer.

Soy sauce, miso and pickled products contain a large amount of sodium chloride in order to ensure that they can be tranaported long distancea or to achieve varlous purposes such es storage, preservation or good manufacturing practice. The filter film of the present invention is capable of allowing the sodium chloride content of these food products to be lowered without impairing their taste.

In producing processed meat products such as hams and sausagea, the meat wrapped in a semipermeabfe membrane must be smoked. Conventionally, the semipermeable membrane ia formed of regenereted cellulose, cellulose derivatives, elginates, collagen, or sheep or bovine gut. However, as already mentioned, these materials heve problema in terms of their physical strength and heat resistance, and in particular, sheep and bovine guts are nof uniform in size and shape and suffer from instability in supply.

Fibrous products are usually porous and the filma prepared by impregnating or coating them with the edible composition of the present Invention serve aa ideal casing materials wherein the semipermeable membrane formed of the edible material isreinforced with the fibrous product. Such casing materials may be prepared as follows: a fibrous product of a given width is shaped into a tubular base, which la continuously impregnated with an aqueous solution of the composition of the present invention and dried to form a strong fibrous casing.

The shelf of conventional soft capsules is formed from an aqueous solution of gelatin and glycerin and is only capable of confining oily products. The soft capsules formed from an aqueous solution of the composition of the present invention are capable of confining not only oily products but also water-soluble substancea and, hence, are applicable to enlarged areas of use, for instance: (1) water-soluble vitamins such as vitamins B_1, B_2, B_5, B_6, B_{12}, niacin folic ecid and vitamin C; (2) nutrients such as fiquid glycides, proteins and minerals; (3) diets formed of soft capsules that incorporete liquid seasonings or flavors and which are readily edible after cooking ; and (4) cosmetics in soft capsules that are to be punctured with a needle to allow the contents to be used.

Soft capsules may be prepared from the composition of the present Invention as follows : the composition is dissolved in weter and the solution la allowed to flow out of e spreader box to form e gef which is subsequently shaped into a film form, two sheets of the film thua obtained are passed through e pair of die rolls to adhere to each other ; a predetermined amount of the content (ie, fill) is forced with e pump to obtain a caplule form, which is subsequently dried to form a soft capsule.

The film prepared in accordance with the present invention is also useful as an ideal wound dressing. It swells readily upon absorbing body fluids from a wounded site of the human body but its three-dimensional network will remain intact. The film increasea in thickness but its area remains the same so as to allow the ebsorbed moisture to be evaporated from its furface. The film supplies the wound surface not only with moisture but elso with the drug applied onto the outer surface of the film ; et the same time, the film allows the unwanted exudate to be liberated on its surface. Therefore, the film doea not have to be peeled off until after the wound has healed. The thickness of the film used as a wound dressing generally ranges from 1 to 1,000μm, preferabfy form 5 to 200 μm, more preferably from 7 to 50 μm.

When the composition of the present invention is dissolved in water, a vicous solution or slurry with a solids content of 2-10 % will form and this can be incorporated in a large amount in suitable food materials. The incorporated composition wilf solidify irreversibly be being left to stand at ordinary temperatures, frozen, refrigerated or heated. The properties, in particular the strength, heat resistance and the temperature for dissolution in water of the solidified product can be altered by properly adjusting the combination of starting materials used. Furthermore, the solidifed product retains the tast flavor of the food material present.

The food materials that can be mixed with the viscous solution or paste of the composition of the present Invention are diverse and include: seaweeds ; marine products such as shrimp, cuttlefish, fish (e.g. bonito, tune and salmon) , and fish roe; vegitables such as spinach, cabbage, carrot and pumpkin; fruits such as orange, grape, apple and pineapple ; meats such as beef, pork, chicken, and comed beef ; processed fooda such as cheese, jam, mayonnaise and miso ; seasonings such as soy sauce and sodium glutamate ; as well as spices and flavors auch as peanut, almond, mustard, pepper, curry, cocoa, coffee an chocolate.

These food materials may be mixed with the viscous solution or slurry of the composition of the present invention either directly, or after being conditioned for a given particle size or shape, or after being formed into a peste. The mixing ratio of these food material to the glucomannan /polyhydric alcohol composition of

the present invention is not limited to any particular value because it largely depends on the type of food material used or the specific formulation of the composition. It should however be noted that e preferable mixing retio is such that the mixture can be readily formed into a film, and that the sheped food is easy to handle end does not reveal the mouth feel of the composition.

The aqueous solution of the composition of the present invention is viscous and its properties, in particular its strength, heat resistance end temperature for dissolution in water, can be eltered by ellowing it to stand at ordinary temperatures, freezing, refrigerating or heating the same. Therefore, the aqueous eolution, after being shaped into e gelled block of an appropriete hardnees, may be mixed with a non-alcoholic beverege such as juice or yogurt or foode, end the resulting mixture can be safely heated without melting to thereby provide a composite dietary product that shows e desireble combination heving the sort of mouth feed that ia possessed by dissimilar components. There is no perticular limitation on the size of the gel block and its hardness varies with the type of base used: if the base is e liquid material such as juice, the moisture content of the block is preferably increased to provide a soft texture, whereas if the base is jelly or any other material that has e certain amount of self-reteining property, its moisture content is decreased to provide a hardness slightly lower than thet of the jelly. In either case, the resulting product is composed to two dissimilar materials and yet displays good palatability.

Glucomannan has a complex structure containing various side chains and reactive groups and, because of the presence of many hydroxyl groups at high concentrations, glucomannan entere into reection to form e complex matrix even under e substantially water-free condition. The matrix forming reaction will be enhanced by the presence of an alkali and an even more complex compound will form. In the presence of both an elkall and water, the development of e three-dimensional network is further promoted to form an irreversibly solidified product, which can be processed to provide e characteristic gel-like base or a coating.

The present invention le hereinafter described in greater detail with reference to the following examples to which the scope of the invention is by no means limited and wherein all parts are on e weight basis.

EXAMPLE 1

Eight parts of glucomannan was mixed with 2 parts of glycerin for 15 minuites an 70 °C to form a sample of the composition of the present invention which wes e somewhet moist powder. Two parts and a half of this composition were mixed with 97.5 parts of water to form a viscous equeous solution. This solution was coated onto the peel of orange and dried at 50 °C for 1 hour to provide orange having an edible film coating on its peel. This orange and uncoated orange were stored et 25 °C for 10 days. Thereafter, the appearance of the two oranges and the mouth feel of their pulp were compared. Compared with the uncoated orange, the one having an edible film coat hed undergone a smeller degree of water eveporation and oxidation, retained more luster and experienced less surface discoloration. The pulp of the coated orange was fresher and more paletable.

EXAMPLE 2

Three parts of the composition prepared in Example 1 was mixed with 0.04 parts of a vitamin E powder (70% natural vitamin E and 30 % emulsifier) and 97 parts of watar to form an aqueous solution. An orange whose peel was coated with the resulting aqueous solution as in Example 1 was stored et 25 °C for 15 days together with an uncoated orange. The results of comparison of the two oranges were the same as in Example 1.

EXAMPLES 3 - 10

The components listed in Table 1 were mixed for 10 minutes et 80 °C in the amounts also shown in Table 1, so as to prepare eight additional samples of the composition of the present invention. Three parts of each of the samplee was mixed with 97 parts of water end the resulting equeoue solutions were cast by the wet process to form translucent edible films having thicknesses ranging from 10 to 20 µm. The films prepared in Examples 3 to 6 were water-resistant end stable in the following eolutions: aqueous solutions with NaCl concentrations of 5% or more ; acidic aqueous solutione with pH of 2.5 - 4.5; alkaline equeous sloutions with pH of 9.0 - 12.0 ; aqueous solutions with ethanol concentrations of 10 % or more. The films prepared in Examples 7 - 10 were not only weter-resistant; they were resistant to hot water and stable in aqueous solutions heated to 80 - 100 °C.

Table 1

(unit in parts by weight)

Example No.		3	4	5	6	7	8	9	10
natural polysaccharide	glucomannan	5	5	5	5	5	5	5	5
	carragaenan	3			2		4		3
	agar		2					1	
	locust bean gue			2					1
	xanthan gue				1		0.5		
alkali	caicium carbonate							0.3	0.1
	calcium hydroxida					0.05			
	sodium bicarbonate						0.5		0.3
glycerin			1.5		1.5	1		1	
sorbitol (70% aq.sol.)		1.5					1		
saccharosa (80% aq. sol.)				1.5					1

EXAMPLE 11

An edible package film 15 µm thick was formed from a composition having the same formulation as used in Example 3. Stripped lobster (150g) was wrapped with this film and stored at-25°C for 3 months. The frozen lobster as wrapped in the film was thawed in a microwave oven and cooked. The cooked lobster had the edible film on it but one did not sense any peculiar feel as e result of the presence of the film.

EXAMPLE 12

An edible film 15µm thick was formed from a composition having the same formulation es used in Example 8. Vegitable selad with dressing was sandwiched between two slices of bread. During subsequent storage, the dressing did not permeate into the bread at all. After the strage, the bread was eaten ; it tasted good and the taste of the edible film was not sensed.

EXAMPLE 13

Components	Amount (in parts)
Glucomannan	5
Sodium bicarbonate	0.1
Calcium Carbonate	0.02
Glycerin	1

These components were mixed at 75°C for 20 minutes. Three parts of the resulting composition were dissolved in 97 parts of water. The aqueous solution was applied continuously to form a uniform coating on the inner aurface e fluoroethylen resin-coated cylindrical pipe having a diameter of 120 mm. The applied coat was dried to form a tubular casing.

Processed meat was packed into the casing at a pressure of up to 2 kg/cm^2 without causing its disruption. The packed meat was smoked and sterilized by heating in hot water (80°C) for 2 hours to produce a satisfactory ham.

EXAMPLE 14

Components	Amount (in parts)
Glucomannan	5
Agar	0.5
Calcium carbonate	0.5
Sodium citrate	0.3
Sorbitol (70% aq. sol.)	1

These components were mixed et 80°C for 10 minutes. Three parts end a half of the resulting composition were dissolved in 96.5 parts of water to form s viscous aqueous solution. A sheet of porous paper having a thicknesa of 100 µm was prepared, with wood pulp and cotton linter being used as chief components. The two side edges of the sheet were adhered together to form a tubular base. The wall of this base was impregnated with the previously prepared viscous aqueous solution and dried to torm a casing that was formed of a sample of the film of the present invention that had a thickness of 120 -130 µm and which was reinforced with a fibrous product.

Processed meat was packed into the casing at a pressure of up to 6 kg/cm^2 without causing its diaruption. The packed meat was smoked and sterilized by heating in hot water (80°C) for 2 hours to produce a satisfactory aausage.

EXAMPLE 16

A mixture of gelatin (100 parts) and glycerin (30 parts) was dissolved in 60 parts of water at 75°C with stirring and defoamed with a vacuum pump. The aolution was shaped into a 450 µm thick film on an automatic rotary continuous soft capsule filling machine. A film 25 µm thick that was prepared asin Example 6 was stacked on the inside surface of the 450 µm thick film to form a double-layered film. Two units of this double-leyered film were passed between a pair of die rolls to be adhered to each other and an aqueous solution of 30% L-ascorbic acid was forced in with a filling pump to form capsules each containing 500 mg of the fill. The capsules were dried to produce soft capsules.

EXAMPLE 16

Components	Amount (in parts)
Glucomannan	5
Carrageenan	0.5
Calcium carbonate	0.12
Glycerin	1

These components were mixed et 70°C for 30 minutes. Three parts of the resulting composition was dissolved in 97 parts of water to form a viscous aqueous solution. the solution was formed into an edible film 15 µm thick by tha wet casting method. As in Example 15, a dual-layered capsule shell was formed by staking this film over a galatin film. Using this shell, soft capsules aach containing 5 g of seasonings for instant chickan soup wera produced. On of these capsules was mixed well with 150 ml of hot water (90°C) under agitation ; the capsule was disintegrated in the water to provide chicken soup.

EXAMPLE 17

A mixture of gelain (100 parts) and glycerin (30 parts) was dissolved in 10 parts of water at 75°C with stirring. Thasolution was defoamed with a vacuum pump and designated A. In a separate step, 5 parts of glucomannan, 3.5 parts of carrageenan and 1.5 parts of glycerin wera mixed at 70°C to form a sample of the composition of tha presnet invention ; 3 parts of the composition was dissolved in 97 parts of water to form an aqueous solution which was dasignated B. An intimate bland of solution A (60 parts) and solution B (40 parts) was fed into an automatic rotary continuous soft capsule filling machine to form soft No. 5 oval capsules by the known rotary die method, with each capsule having confined therein 290 mg of an astringent lotion. Just prior to use, each soft capsule was punctured with a needle to recover to lotion in an amount sufficient for singla use.

EXAMPLE 18

Components	Amount (in parts)
Glucomannan	5
Carrageenan	3
Cellulose	1
Glycerin	2

Thase componants were mixed at 80°C for 10 minutes and 2.5 parts of the resulting composition was dissolved in 97 parts of wetar. The solution was formad into a circular film (thicknass, 15 µm ; diameter, 29 mm) by tha wat cesting method. Tha film was set in a filtrstion vassel which was filled with 450 ml of tap water in its lower compartment and with 150 ml of soy aauca (18% NaCl) in its upper compartmant. Tha vessel was left to stand at 20 °C for a givan period and the contents of NaCl and amino acid nitrogan in the soy sauce were measured at predetermined intervals. Tha results are shown in Table 2.

Table 2

(effective surface area of film: 960.6 mm²)

Time (min)	NaCl (%)	Amino acid N_2	Increase in water content (%)
0	16.4	0.91	0
30	15.7	0.86	0.7
60	16.5	0.82	1.6
90	15.0	0.86	2.7
120	14.1	0.79	4.1
150	13.3	0.78	5.7

As Table 2 shows, the NaCl content of the soy sauce decreased with time and this was accompanied by gradual depletion of amino acids and increase in the moisture content. However, most of the amino ecids that flowed out were those having low molecular weights such as glycin and alanine and their depletion did not cause any substantial deterioration of the taste of the soy seuce. The soy sauce prepared in accordance with the present invention had e generally mellow taste and its sodium chloride content was low.

EXAMPLE 19

An aqueous solution of the composition used in Example 18 was heated to 70 °C with stirring and applied to a thin sheet of paper (basis weight: 16g / m²) to form a film having a thickness of 35µm. This fiber-reinforced film was tested as in Example 18. The results were substantially the same as those obtained in Example 18. The film prepared in this example was superior to that prepared in Example 18 in terms of self-retaining property end tensile strength.

EXAMPLE 20

Components	Amount (in parts)
Glucomannan	5
Xanthan gum	0.5
Calcium hydroxide	0.06
Glycerin	1

These components were mixed et 60°C for 20 minuites to obtain e sample of the composition of the present invention. Three parts of this composition were dissolved in 97 parts of water and a thin leyer of the solution was spread onto a fluoroethylen resin-coated sheet. The coating was freeze-dried by e conventional method to prepared e wound dressing in a film form having a thickness of 12 µm. The film wes sterilized, coated with e drug leyer and attached to the surface of a wound produced by e third-degree burn. The treatment thet ensured consisted of delivering the drug dally onto the surfece of the film. Formation of granuletions continued steadily without suppuretion and In 10 deys normel skin tissue was restored,

whereupon the film separated from the skin spontaneously.

EXAMPLE 21

An aqueous solution of the composition used in Example 20 was coated onto e nonwoven polyester fabric (basis weight : 10g / m^2) and freeze-dried by a known method so as to make e film heving a thickness of 30µm. This film was used as a wound dressing to cure a burn in eccordance with the same regimen as employed Example 20. The results were substantially the same as those obtained in Example 20.

EXAMPLE 22

Components	Amount (in parts)
Glucomannan	5
Alginic acid	1
Guar gum	0.5
Glycerin	1

These components were mixed at 65°C for 20 minutes to form a sample of the composition of the present invention. Three partsof this composition were dissolved in 97 parts of water. Seventyfive parts of the solution were mixed with 25 parts of a beef fillet and the blend was shaped into an edible film (thickness : 25µm) by the wet casting method. The film was laid down on a slice of bread ; the product had a characteristic flevor originating from the blending of the taste of beef with the bread.

EXAMPLE 23

Components	Amount (in parts)
Glucomannan	5
Tamarind seed polysaccharide	1
Gelatin	1
Glucose (80% aq. sol.)	1

Theee components were mixed et 60°C for 40 minuites to form a sample of the composition of the present invention. Three parts of this composition were dissolved in 97 parts of water to form a viscous aqueous solution. Eighty parts of this solution were blended with 20 parts of e dried spinach powder (particle size : 100-Tylermesh pass) snd the blend was shaped into an edible film (15µm thick) by e known freeze-drying technique. This film was rolled eround a bar of cooked rice so as to provide e low-calorie dietary product.

EXAMPLE 24

Components	Amount (in parts)
Glucomannan	5
Carrageenan	5
Calcium carbonate	0.2
Glycerin	1.5

These components were mixed at 70 °C for 30 minutes to form a sample of the composition of the present invention. Five parts of this composition were mixed and kneaded with 95 parts of cocoa paste and the necessary seasonings to make a chocolate mass, which was refined and molded into a sheet. Although conventional chocolate products are soften at 35 °C or higher, the chocolate sheet of the Example 24 did not soften until it was heated to 50 °C.

Claims

1. A glucomannan/polyhydric alcohol composition prepared by uniformly mixing at 5 to 150 °C 1 part by weight of a glucomannan powder with 0,05 to 10 parts by weight of an aqueous solution of 30-100 wt.-% of at least one polyhydric alcohol selected from the group consisting of propylene glycol, glycerin, sugar alcohols, monosaccharides, disaccharides and oligosaccharides.

2. A composition according to claim 1, characterized in that the components are mixed in the presence of an alkali.

3. A composition according to claim 1 or 2 wherein part of the glucomannan is replaced by another natural polysaccharide.

4. A composition according to claim 3, wherein the other natural polysaccharide is carrageenan.

5. A film prepared by a process comprising the steps of: dissolving a glucomannan/polyhydric alcohol composition according to anyone of the claims 1 to 4 in water, forming the solution into a film by shaping it into a solidified form of a suitable thickness between 1 and 1000 µm by any of the known techniques, and drying the film.

6. A film according to cleim 5, characterized in thet it is edible.

7. A film according to claim 5 or 6 which is reinforced with a thin fibrous product.

8. The use of a film according to anyone of the claims 5 to 7 as a food packaging.

9. The use of a film according to anyone of the claims 5 to 7 as a casing in the manufacture of smoked food products.

10. The use of a film according to anyone of the claims 5 to 7 as a shell of a soft capsule.

11. The use of a film according to enyone of the claims 5 to 7 as a semipermeable membrane for separating a high-molecular weight substance from a low-molecular weight substance.

12. The use of a film according to anyone of the claims 5 to 7 as a wound dressing.

Patentanaprüche

1. Glucomannan/mehrwertiger Alkohol-Zusammensetzung, erhalten durch gleichförmiges Vermischen bei

5 bis 150 °C von 1 Gew.-Teil eines Glucomannenpulvers mit 0,05 bis 10 Gew.-Teilen einer wäßrigen Lösung von 30 bis 100 Gew.-% mindestens eines mehrwertigen Alkohols, ausgewählt aus der aus Propylenglykol, Glycerin, Zuckeralkoholen, Monosacchariden, Disacchariden und Oligosacchariden bestehenden Gruppe.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß die Komponenten in Gegenwart von Alkali vermischt werden.

3. Zusammensetzung nach Anspruch 1 oder 2, bei der ein Teil des Glucomannans durch ein anderes, natürliches Polysaccharid ersetzt ist.

4. Zusammensetzung nach Anspruch 3, bei der das andere natürliche Polysaccharid Carrageen ist.

5. Film bzw. Folie, erhalten durch ein Verfahren, das die Schritte umfaßt:
Auflösen einer Glucomannan/mehrwertiger Alkohol-Zusammensetzung gemäß einem beliebigen der Ansprüche 1 bis 4 in Wasser,
Überführung der Lösung in einen Film bzw. eine Folie durch Überführen derselben in eine verfestigte Form mit einer geeigneten Dicke zwischen 1 und 1000 µm durch eine beliebige, bekannte Arbeitsweise,
und
Trocknen des Films bzw. der Folie.

6. Film bzw. Folie nach Anspruch 5, dadurch gekennzeichnet, daß er bzw. sie eßbar ist.

7. Film bzw. Folie nach Anspruch 5 oder 6, der bzw. die mit einem dünnen, faserförmigen Produkt verstärkt ist.

8. Verwendung eines Films bzw. einer Folie gemäß einem beliebigen der Ansprüche 5 bis 7 als Verpackung für Lebensmittel.

9. Verwendung eines Films bzw. einer Folie gemäß einem beliebigen der Ansprüche 5 bis 7 als Umhüllung bei der Herstellung von geräucherten Lebensmitteln.

10. Verwendung eines Films bzw. einer Folie gemäß einem beliebigen der Ansprüche 5 bis 7 als Hülle einer Weichkapsel.

11. Verwendung eines Films bzw. einer Folie gemäß einem beliebigen der Ansprüche 5 bis 7 als semipermeable Membran zur Abtrennung einer Substanz mit hohem Molekulargewicht von einer Substanz mit niedrigem Molekulargewicht.

12. Verwendung eines Films bzw. einer Folie gemäß einem beliebigen der Ansprüche 5 bis 7 als Wundverband bzw. Wundabdeckung.

Revendications

1. Composition à base de glucomannan et d'alcool polyhydrique, préparée en mélangeant uniformément à la température de 5 à 150 °C, une partie en poids de poudre de glucomannan avec 0,05 à 10 parties en poids d'une solution aqueuse de 30-100% en poids d'eau moins un alcool polyhydrique, choisi parmi le groupe comportant propylène glycol, glycérine, alcools de sucres, monosaccharides, disaccharides et oligosaccharides.

2. Composition selon la revendication 1, caractérisée en ce que les composants sont mélangés en présence d'un alcali.

3. Composition selon la revendication 1 ou 2, dans laquelle une partie du glucomannan est remplacée par un autre polysaccharide naturel.

4. Composition selon la revendication 3, dans laquelle l'autre polysaccharide naturel est le carregeenan.

5. Film préparé par un procédé comprenant les étapes de :
dissoudre une composition à base de glucomannan et d'alcool polyhydrique selon l'une quelconque des revendications 1 à 4, dans l'eau, former avec eolution un film en le traitant dans une forme solidifiée, d'une épaisseur convenable, entre 1 et 1000 µm par n'importe quelle technique connue, et sécher le film.

6. Film selon la revendication 5, caractérisé en ce qu'il est comestible.

7. Film selon la revendication 5 ou 6, qui est renforcé avec un produit fibreux mince.

8. Utilisation d'un film selon l'une quelconque des revendicatione 5 à 7, comme emballage de nourriture.

9. Utilisation d'un film selon l'une quelconque des revendications 5 à 7, comme emballage dans la fabrication des produits alimentaires fumés.

10. Utilisation d'un film selon l'une quelconque des revendications 5 à 7, comme enveloppe d'une capsule molle.

11. Utilisation d'un film selon l'une quelconque des revendications 5 à 7, comme membrane semiperméable pour séparer une substance de poids moléculaire élevé d'une substance de faible poids moléculaire.

12. Utilisation d'un film selon l'une quelconque des revendications 5 à 7, comme pansement d'une plaie.